USGS

WATER RESOURCES RESEARCH GRANT PROPOSAL

Title: Spherical Cavity Ring-down Spectroscopy of Water

Focus Categories: Methods, Water Quality

Keywords: Ring-down spectroscopy, whispering-gallery mode, water quality control

Duration of Project: March 1, 2000 to February 28, 2001

FY 2000 Federal Funds:

$9,556	($9,556)	(0)
(Total)	Direct	Indirect

FY 2000 Non-Federal Matching Funds Committed:

$19,193	($16,049)	($3,144)
(Total)	Direct	Indirect

Principal Investigator's Name and University:

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Water Resource Institute: Tennessee

Congressional District: Third congressional district (Hamilton County)

Statement of Critical Regional Water Problem

Chemical measurement techniques are central to water quality control. The ability to sensitively, accurately, precisely, rapidly, and conveniently determine the presence of foreign species in natural waters allows for potential control of pollution sources and the verification of regulations. The goal of this research project is to develop a highly sensitive spectroscopy using an ultrafast pulsed laser and the spherical cavity-ringdown technique for fast and sensitive detection of pollutants in water. The method will be especially useful in dealing with radioactive pollutants in the Watts Bar lake and the Clinch River area, where the pollutants are low in concentration but highly hazardous. The technique should be beneficial to water quality control agencies.

Two scenarios are envisioned. In the first, our measurement sensitivity would exceed the best current methods. Thus, earlier detection of problems (e.g., industrial effluent) could be achieved or more stringent regulation compliance could be validated. Current sensitive methods are laboratory-based, and collected samples must be returned to some facility for analysis. In the second scenario, the use of cavity ringdown in spheres might only result in sensitivity comparable to laboratory-based methods, but might be amenable to field use. Our ultrafast pulse lasers are currently far from field-deployable, but new developments in laser technology are occurring at a rapid rate. Fiber optic lasers capable of generating ultrafast light pulses are currently commercially available and might be useful for these measurements. A strong driving force for further laser improvements is that the same parameters important for our needs apply to optical communications needs, as well. Thus, a consumer, rather than a scientific, market will set the development pace.

Research Results, Benefits and/or Information

This project should provide an improved design of the cavity ringdown spectrometer for sensitive absorption spectroscopy. The results will be submitted to the Water Resource Center and to a refereed journal for publication.

Nature, Scope and Objectives of Research

Chemical measurement techniques are central to water quality control. The ability to sensitively, accurately, precisely, rapidly, and conveniently determine the presence of foreign species in natural waters allows for potential control of pollution sources and the verification of regulations. The goal of this research project is to develop an optical absorption technique for the sensitive measurement of chemicals in water. Detection of optical absorption is as old as the perception of color. Optical absorption in the visible spectral range is, indeed, the origin of color for transparent materials. For use as a quantitative technique, however, wavelength selectivity and instrumental recording must be added to simple visual observation. These enhancements have enjoyed continuous evolution throughout this century.

For convenience, a method to measure trace constituents must be applicable without any sample pre-concentration steps, that is, a collected water sample must be suitable for measurement as is, without any preliminary steps. Thus the measurement technique must exhibit adequate sensitivity. Accurate detection of a 1% attenuation is a reasonable measurement goal. For a 1-cm solution path length and a typical molecular absorptivity of approximately 5000, that limits us to solutions with micromolar (mM) concentrations and higher. Of course, the measurement path length can be increased, and some analytes exhibit absorptivities higher than 5000; the mM limit is intended to represent a general limit. Fluorescence spectroscopy can be substantially more sensitive, but many species do not fluoresce and thus are not amenable to measurement using that technique. Any improvements that can be attained to reduce the detection limit for absorption spectroscopy would allow for more sensitive direct determination of pollutants. Some examples of such improvements include the use of colorimetric reagents that yield much higher molar absorptivities in the presence of target pollutants and methods that do not require quantification of a small attenuation of a transmitted light level. An example of the latter would be photoacoustic spectroscopy.

We have studied the propagation of ultrashort light pulses with durations as short as 2 picoseconds (i.e., 2×10^{-12} seconds) in spherical dielectric cavities. The cavity modes in these devices are analogous to the whispering gallery modes (WGM) of acoustics. The light travels around the sphere circumference, just at the interface between the sphere and its surroundings. The light path can be described as an inscribed polygon, in a ray optics construct. While the pulse is totally internally reflected at each reflection apex, leakage of a small fraction of the light does occur and can be detected using a properly oriented, fast photodiode. Thus, whereas a single light pulse is injected into the sphere, the detector records a train of pulses, separated by the round-trip time in the sphere at the speed of light.

We are attempting to extend these experiments to liquid spheres, wherein the light would be slightly absorbed on each transit around the sphere, if the liquid contains a weak absorber. Thus each pulse in the train would be slightly less intense than its predecessor, and the overall wave packet would be described as a decaying exponential. Quantification would be accomplished by fitting the decay to an exponential and comparing the resulting decay time constant with that for the absence of the absorber. This method would have several significant advantages over conventional absorption spectroscopy. First, each attenuation measurement (i.e., pairs of pulses in the train) is based on a single input pulse; thus the source stability is not an issue. Second, the many round trips achieved translate into a very long path length. A 1-cm diameter sphere might correspond to an overall path length of tens of meters. A linear version of this technique has been reported and is termed cavity ringdown spectroscopy (CRDS). In that case, two flat mirrors are employed to surround the absorber and form a linear cavity. Complications of this technique are that the mirrors must be of extremely high reflectivity (>99.99%) and must be carefully aligned to achieve near perfect retro-reflection on each pass.

Several experimental embodiments are available to achieve the spherical liquid geometry required for the measurements described above. The most direct would be to employ a water drop. Unfortunately, coupling light into a free water drop results in extremely leaky WGMs, and the propagating pulse decays away too rapidly. Touching the drop to a coupling prism solves this problem by changing the WGM orders achievable, but so severely distorts the drop from sphericity that it will not support WGMs. Another geometry we have explored in some preliminary experiments was a hollow glassblown sphere that was ground flat at an equator, just to the point of breaking through the wall. That small opening then served as an optical coupling point when the vessel was glued to a high refractive index prism. Some success has been observed using this method, but severe constraints apply to the permissible values for the liquid refractive index, and only a few solvents are acceptable, not including water.

We wish to explore two additional approaches to this problem. The first uses thin wall vessels that will support hybrid WGMs, even when water (n=1.33) is the solvent. In this case, total internal reflection will occur at the glass/air interface at the outside diameter of the vessel (as opposed to the liquid/glass interface). This explains why in this case the water refractive index would be acceptable. The second approach is to employ glass spheres that have been coated with a material (e.g., a polymer doped with a colorimetric reagent) that can be exposed to liquid solutions. In this case, pulses will propagate in WGMs the solid phase, as occurred during our earlier glass sphere experiments, but the color change induced in the doped coating by the analyte will provide the optical attenuation to be measured.

Objective

In this project, we plan to accomplish two tasks at the Oak Ridge National Laboratory. We will be able to utilize existing equipment there and work in collaboration with Dr. Robert W. Shaw in the Chemical and Analytical Sciences Division. The two tasks are:

> 1) Improve the spherical bottle - prism method to achieve stable whispering-gallery modes in liquid carbon disulfide. The time-domain absorption of liquid within a spherical glass bottle will be measured. The absorption measurement will be conducted for solutions with different concentrations of $NdCl_3$ which have distinctively different absorption constants within the tuning range of the laser wavelength. The decay constants of the different solutions will be deduced and related to the corresponding concentrations. These experiments will help to fix the geometry of the optics, improve and test the software.
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> Completion Date: August 31, 2000.
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> 2) Use thin wall vessels that will support hybrid WGMs, even when water (n=1.33) is the solvent. Total internal reflection will occur at the glass/air interface at the outside diameter of the vessel. This approach is attractive because it can provide a convenient means of water pollutant detection, although there are challenges such as ways to cope with the multi reflection between the two walls of the glass bottle. A possible solution may be an anti-reflection coating on the inner surface. The outer surface of the glass bottle can be coated with metal to increase the reflectivity.
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> Completion Date: February 28, 2001.

Experimental Methods, Procedures and Facilities

With the exception of minor supplies, the equipment for these experiments exists within the Chemical and Analytical Sciences Division at Oak Ridge National Laboratory.

Experimental time and equipment access will be provided to us, in that the proposed research will be a collaborative effort with Dr. Robert W. Shaw.

The experimental set-up is shown in Figure 1. Two-picosecond duration pulses near 795 nm at 76 MHz are generated using a Kerr lens mode-locked titanium:sapphire laser with an average power of approximately 1 watt. The laser beam is coupled into a liquid sphere through a glass prism with an index of refraction of 1.722. The laser beam is incident into the prism at a certain angle so that complete internal reflection is achieved and a whispering-gallery mode is established in the sphere. Each laser pulse thus generates a train of pulses. The intensity of these pulses decay exponentially as a result of the leakage at the coupling spot and absorption by the liquid. The decay time constant depends on the leakage and the absorption of the liquid, but does not depend on the intensity of the incident laser pulse. Part of the laser pulse circulating around the sphere is coupled out through the prism and imaged onto a fast photodiode (14 ps risetime) and processed with a digital oscilloscope. The digital oscilloscope is interfaced to a PC computer and the data is transferred into the computer for analysis. The pulse width is accurately measured with an autocorrelator. A He-Ne laser is integrated into the system to aid the alignment.

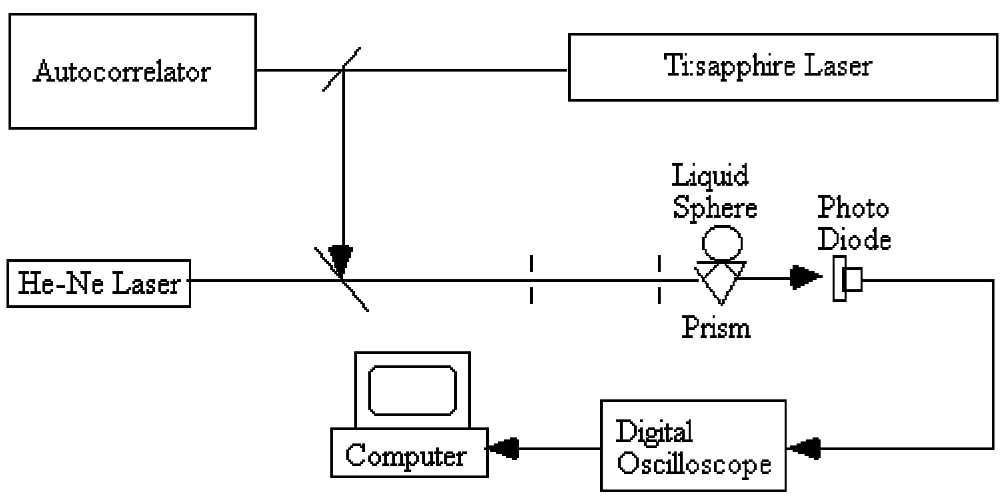

Figure 1. Experimental Set-up

Related Research

1. J.B. Paul and R.J. Saykally, Anal. Chem. **69**, 287A (1997). Paul and Saykally studied linear cavity ringdown spectroscopy (CRDS) for sensitive analysis of chemicals. In their experiment, two flat mirrors are employed to surround the absorber and form a linear cavity. Complications of this technique are that the mirrors must be of extremely high reflectivity (>99.99%) and must be carefully aligned to achieve near perfect retro-reflection on each pass. In our experiment, the cavity ringdown is achieved through the total internal reflection of the light beam on a spherical surface which also serves as the

focusing device. The high reflectivity is guaranteed as long as the index of refraction of the sphere is greater than that of the surrounding medium and the angle of incidence is greater than the critical angle.

2. R.W. Shaw, W.B. Whitten, M.D. Barnes, and J.M. Ramsey, Opt. Lett. **23**, 1301 (1998), W.B. Whitten, R.W. Shaw, M.D. Barnes, and J.M. Ramsey, Technical Digest, 7th Laser Application to Chemical and Environmental Analysis, Orlando, FL, March 9-11, 1998, p.55. Shaw et al. studied whispering gallery mode (WGM) propagation in the time domain for optical pulses and macroscopic glass spheres. The whispering gallery modes were achieved in the solid spheres (diameter = 6 to 26 mm) by using a glass prism coupler. This work laid the foundation for application of the technique in cavity ringdown spectroscopy of materials with low absorption rate.

3. R.W. Shaw, W.B. Whitten, M.D. Barnes, and J.M. Ramsey, and L.J. Wang, Spherical Cavity Ringdown Spectroscopy Experiments, to be presented in the Conference of Laser Applications in Chemical and Environmental Analysis on Feb. 11-13, 2000 at Santa Fe, New Mexico. In this paper we reported the preliminary results of applying the cavity ringdown technique to liquids. The future developments are also discussed in the paper. The positive results from this research is a part of the reasons that motivated this proposal. These results also reveal a challenges for applying the technique to practical spectroscopy: a) to effectively couple the laser beam into a liquid sphere and establish whispering gallery modes. b) to find a way to achieve the whispering gallery mode in water. The objective of this proposal is to overcome these challenges.